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Procedia Chemistry 3 (2011) 118–121

Chemistry Procedia

22nd Solvay Conference on Chemistry

Discussions on Session 2B: Quantum effects in chemistry

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R. Marcus: I thought that was extremely interesting, David, and I have two questions: one concerns that gap of 4 Å. Because that path is so small the water molecule didn't reach there, wasn't the water molecule able to fill the gap?

D. Beratan: Which system are you referring to?

R. Marcus: Where you showed the shorter pathway and you pointed out that there is a gap there and I was wondering: are there those gaps in proteins because of the water molecules?

D. Beratan: That gap I showed in cytochrome *c* was more or less a van der Waals contact so that there was no room for water to enter there. But there are gaps in other protein systems where there is indeed sufficient space to fill with water, and that needs to be and is taken into account in the calculations. We include that water in our analysis now and we do the best we can to simulate those waters and their dynamics. This issue on how waters contribute in detail to the reaction coordinate, the tunneling barrier, and the correlation among the two is largely an open one.

R. Marcus: My second question: I was intrigued by your noting that one term dominated when something was more than 6 Å and I asked Graham what is the typical size of an amino acid, and that is 5 Å. I remember quite a few years ago, we looked at pathways in proteins where the individual units were amino acids and the perturbation coupling between the units was small. Now if you think of the paths as being amino acid paths, you come up with your conclusions.

D. Beratan: Indeed, what we find is that on the scale of a single amino acid, i.e. 5-7 Å, a limited pathway depiction would be fine in many cases. But when you start going to larger distances, and this is a statistical statement, you begin to have multiple pathway effects that probably average out some of the pure strongest single pathway effects that we have described. We think the secondary structure features persist despite the fluctuations - they don't get erased - but some of the fine points of the strongest single pathway probably get averaged out. I haven't thought about making coarser-grained single amino acids models - that might be fun to try and do - and it may be appropriate for those shorter distance regimes, but we would have to take orientation effects into account.

A. Nitzan: This is a question to Prof. Kauffmann about the exciton-phonon coupling, you emphasized the delocalized nature of the excitons and intuitively I think that coupling to vibrations is very local but some of your experiments indicate otherwise. Could you explain it?

Selection and/or peer-review under responsibility of G.R. Fleming, G.D. Scholes and A. De Wit
doi:10.1016/j.proche.2011.08.018

H. Kauffmann: First of all, in principle we have no experiment currently feasible of that. The difference was quite evident in the first picture where we saw in the aggregate which is an electronic oscillator that, in a very early stage, these oscillations were quite evident. The antidiagonal was involved and this is the location for homogeneous broadening. On this basis we were now interested in what is the role of vibrational modulations by means of a long wavelength of a nuclear mode or a very high frequency. So we investigated both but we used a single chromophore system. So we definitively used a system knowing that we are dealing now with a localized situation in order to learn about the dimer where there is indeed a theory of Professor Fleming. Thomas Mancal was also involved and it is now also our theoretician who is thinking on how we can tackle the problem of electronic vibronic packets and their role in energy transfer. I have a couple of interesting biochemical materials where I can e.g. show the carotene-purpurin energy transfer were we see e.g. in the very early regime for t_2=0 the unperturbed exciton, but when we looked at 10 fs or 20 fs, then we see that it is totally dominated and concealed by excited state absorption processes and no longer by stimulated emission processes. Due to the complexity of the purpurin and the carotene system, there is a concealing and overlapping effect where we cannot look through, so it is important to polarize the spectra or polarize the pulses in order to learn a little bit whether we can influence the positions of the diagonals in order to get the off-diagonals free. I have one experiment but I am limited in time so I didn't present it. I can present it but it is a little bit outside the format.

J. Knoester: It is quite clear that the excitation is quite delocalized and we have a lot of information that it is, and the disorder is really not that large and the band width is quite large so the excitations have to be quite delocalized. The vibronic coupling for these systems is actually rather small if you look at the linear absorption spectrum, you don't see a lot of progression and even for the single molecule you see very little progression so there is all kind of information that the vibronic coupling is very small.

H. Kauffmann: On the other hand, from a chemical argumentation one has to say definively that the monomeric system is indeed a weakly coupled system but it is clear that disorder is an elementary reason to introduce and without disorder it was not possible to fit the data. The second point is, as you saw, that you have an extreme streaking line. This comes from the higher density of states by releasing the populations that will then couple again with the lower one and then definitely you have a stream of population that goes down and at longer time also upward, both. So from this point of view the motivation was to look in these systems. I agree with you on that respect that if you would have used pulses which were not so short we wouldn't have overlap, this is clear, so in this case it is not so good to employ these extreme broad pulses.

T. Renger: I have a question for Prof. Beratan. You mentioned that when you excite the bridge vibrationally, the electron transfer rate drops down by a factor of 3. Could one understand that as introducing pure dephasing in the bridge that effectively destroys the coherence between donor and acceptor or is it some other mechanism ?

D. Beratan: That is an interesting suggestion. Our current hypothesis is that the vibrational excitation weakens the hydrogen bonds (gets picture of the molecule up). I don't have a comment to make on the decoherence argument - it is fun to think about. We have a simpler argument and that for vibrational excitation in a relatively broad region of the mid-IR, a good bit of the oscillator strength in that region is in these NH_2 scissoring motions. If you look at the structure of these molecules, scissoring the NH_2's will only weaken the hydrogen bonds, so we imagine that driving these vibrations would weaken the coupling pathways and that's the remark I would make. But there is a very interesting unpublished observation that our collaborator Igor Rubtsov has made. He can not only measure the charge separation from this aromatic amine to the anthryl derivative, but he can also measure the back electron transfer. In fact, the back electron transfer is actually accelerated when the IR impinges on the system, so this gives us more information about how bridge vibrational excitation perturbes electron transfer. We have a lot to explain here and it is really the early days of these three-pulse experiments.

T. Renger: So probably the decoherence would also lead to a lowering of the back transfer?

R.A. Harris: I'd like to comment on the chirality experiment, when you have right circularly polarized light and a right chiral object that is different from a left chiral object. That is not surprising, but are you saying that left with left is different than left with right?

D. Beratan: Let's keep the chirality of the molecule on the surface fixed and let's measure the photoelectron yield for left vs. right circular light and that asymmetry is not zero, there is a 20 % yield asymmetry.

R.A. Harris: But the monomer of the chiral molecule is the same then that, in a way, is like a cd experiment cause the intensity is linear, so in free space this would be like a linear CD emission experiment, so this is not surprising.

D. Beratan: Good. I would add that you can get the same effect with achiral systems, the key to it is to sample of the complex phase of the wave function, so chirality was a central part of their experiment - but it is not an essential part of the physical effect that I have described.

R.A. Harris: It is a constrained surface isn't it, so that breaks the full parity argument.

K. Nelson: Do sub-populations exist with vibrationally excited and not-excited molecules?

D. Beratan: Indeed this is an ensemble experiment in solution and the IR excitation is very broad, so different molecules will be following different trajectories.

K. Nelson: But what I mean is that some electronically excited molecules will be vibrationally excited and some won't be at all so I would expect to see two sub-populations.

D. Beratan: The experiment uses chopped IR excitation, so we can separate the two sub-populations that you mention.

K. Nelson: It may suggest possible mixed experiments of this sort on exciton systems as well and we might speculate on the role that vibrations may play there.

S. Mukamel: A question to Prof. Beratan: you showed this variance in the coupling and this is basically a static expression and it is valid as long as the fluctuations are slow compared to the gap between donor/acceptor and bridge. Is that the case in your system?

D. Beratan: Yes, the timescale of the coupling fluctuations are about 20 fs and the time that you live in this Franck-Condon region is on the scale of single digits of fs. One can have a very interesting timescale discussion but the Franck-Condon approximation seems to work very well in these systems, and we think it is safe to take snapshots and calculate coupling matrix elements for them and do the averaging we describe.

A. Olaya-Castro: I found interesting that when you have local vibrations it seems to leave a mark of the specific route that the electrons have taken. Is this correct?

D. Beratan: Indeed in this particular experiment we are exciting vibrational modes in the part of the molecule that mediates the tunneling.

A. Olaya-Castro: It is interesting because in these molecules it looks like the which-way experiments they are doing in quantum information field.

D. Beratan: That was indeed our motivation, so we wanted to have molecular analogue of double slit experiment. And the direction we are going with this is to build higher symmetry molecules, which come from Jonathan Sessler at UT Austin and we want to design molecules that are more along the lines that Mark showed, rigid π-electron systems where we might imagine isotopically replacing two carbons that participate in a triple bond so that we can have π-symmetry bridges with a local oscillator that we can perturbe and try to do a molecular which-way experiment.

A. Olaya-Castro: In that way there is an analogy with experiments in quantum optics, would it be possible to have more than a single electron transferred?

D. Beratan: So would you like to move them coherently or sequentially?

A. Olaya-Castro: You have experiments here directed to demonstrate interference between pathways. I was wondering if there could be experiments directed to demonstrate correlations between intensities, like a Hanbury, Brown and Twiss experiment, but with electrons.

D. Beratan: The redox species that are stable in redox states differing by two rather than one, Pt e.g., tend to undergo large reorganizations associated with electron transfer. But the question of whether or not you can design experiments that would coherently move two electrons at the same time is an open one, and some of us might have thought about that a little bit, but I don't think it is very well explored.

M.A. Robb: Steven Nielsen has made a compound that might be relevant to this discussion, he has a donor and an acceptor and an aromatic system in the middle in particular a benzene ring, so if you put a positive charge on a benzene ring, you get the lower half of a Mexican hat type of thing and that potential energy system you can go around that both ways. We have done the theoretical calculation and both pathways exist but the differences between them are too great that you could see them in an experimental effect. But I am sure that somebody is clever enough to make an experiment that could do it.

D. Beratan: So what we need is a strategy to leave a marker on the pathway taken, in order to execute this double-slit experiment.

R.D. Cogdell: What about having a molecular system that has two donors and one acceptor, where the donors are symmetrically arranged around the acceptor, then simultaneously excite the two donors.

D. Beratan: We have thought about that, and that's part of our design now. You could think of the double slit in a different way, so that the electron might choose left versus right depending on what you have done to otherwise symmetric bridging groups. That might be a more tractable way to try and pull this off.

J. Knoester: Maybe to bring this discussion a bit to the electronic energy transport side, could you do something similar to what Prof. Beratan was just discussing with electronic energy where you have two pathways that compete with each other and that may interfere with each other, bring energy from point A to point B via two different possible pathways? I have been trying that idea but I don't know of a physical realization of such a system. I once challenged a synthetic chemist in our institute to doing something like that using DNA as a backbone to attach different chromophores with two different possibilities. So does anyone know of such a situation? The complication is that energy transport is usually a much longer range phenomenon such that it may be difficult to select some pathways like you can do in charge transfer.

G. Fleming: We looked for this effect in photosynthetic proteins where you can obviously imagine multiple pathways from one side to another of a protein but I don't think we found any clear examples of it so far but it seems possible so it would be findable in natural systems.

J. Knoester: You have various pathways but the question is: is there interference between them?

D. Beratan: Could I comment on that? I think you can try to do that in Dexter spin forbidden excitation transport (which depends upon molecular coupling pathways) and we are working on now. We think this approach may be possible.

N.B.: Unfortunately Prof. Brumer was unable to attend the conference so there was no direct discussion of his paper.